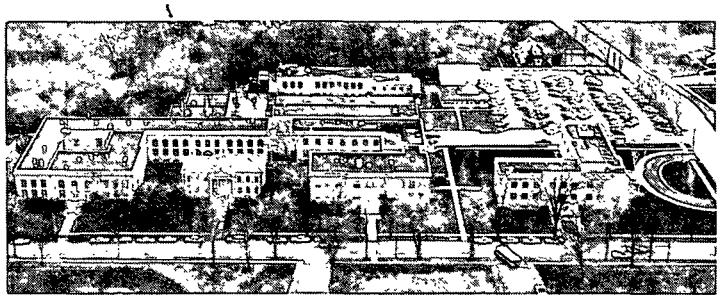

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 131

THE BASICITY OF HYDROXIDE ION AT 170°C

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NOVEMBER, 1982

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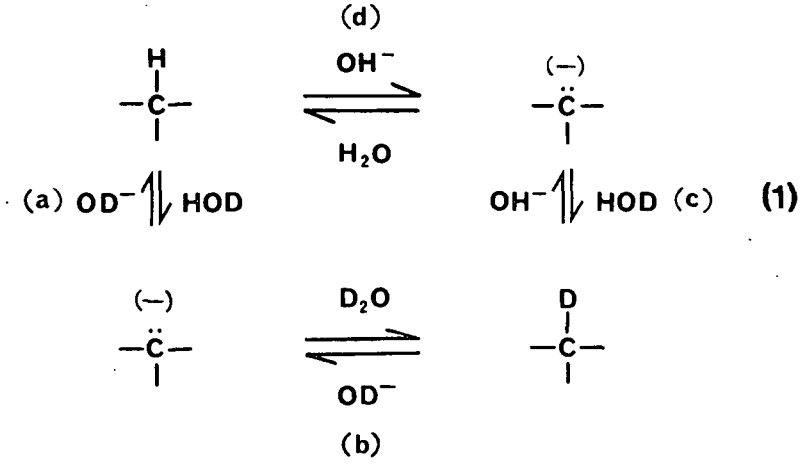
ABSTRACT

The ability of hydroxide ion to produce carbanions at 170° in water has been determined by measuring the extent of deuteration and reexchange of deuterium labels for several organic acids and phenols. It has been estimated that OH^-/H_2O at 170° can deprotonate organic acids having pK_a values of about 35. Compounds such as mandelic acid, p-toluic acid, and p-toluenesulfonic acid and diaryl methanes have been deuterated at their aliphatic carbons with $NaOD/D_2O$ at 170°. The deuterium/proton exchange reactions appear to involve polyanion intermediates. The reactions appear to be useful as a general method of incorporating deuterium labels in alkali insensitive compounds. Several experiments were directed toward understanding the effects of α-hydroxyl groups and zinc ions on carbanion formation. Exchange reactions involving Na_2S at 170° showed that this species is largely dissociated to NaOH and NaSH and that the latter does not contribute to the basicity of the solution.

INTRODUCTION

The chemical pulping of wood often employs strongly alkaline solutions and, in the case of kraft pulping, also sodium sulfide (Na_2S). During pulping roughly one-half of the wood constituents are solubilized either by the action of hydroxide ion (OH^-) as a base or OH^- and SH^- ions as nucleophiles.[1] Some hydroxide reactions also stabilize constituents; for example, the chemical carbohydrate "stopping" reaction[1] appears to be favored by high concentrations of hydroxide.[2,3]

An important aspect of understanding the reactions of wood components during pulping is a fundamental understanding of the basicity of OH^- at 170°. The ability of OH^- to abstract protons from a wood chemical or any organic material will be difficult to observe unless isotopes (deuterium or tritium) are used. However, the use of isotopes has drawbacks. Since OD^- in D_2O is a stronger base than OH^- in H_2O,[4] the former system may produce carbanion (eq. 1a) where the latter would not (eq. 1d). Also, since a C-D bond is stronger than a C-H bond,[5] deuterium removal from a C-D site (eq. 1c) will be more difficult than proton removal from a C-H site (eq. 1d).



If proton exchange at a C-D site can be accomplished, then surely proton exchange at a C-H site can occur for the same substrate. If deuterium exchange is not possible at a C-H site, then surely proton exchange also cannot occur. If, however, deuterium exchange occurs at a C-H site (eq. 1ab), but proton exchange of the analogous C-D site (eq. 1cd) fails, we are on the edge of the ability of OH^- to produce carbanions of this type. Thus, a compound which undergoes deuterium exchange but no proton reexchange provides an example of the limits of OH^- to produce the derived carbanion.

Several methods are available to determine the extent of deuteration; these include mass spectroscopy and both proton (^1H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR). The NMR

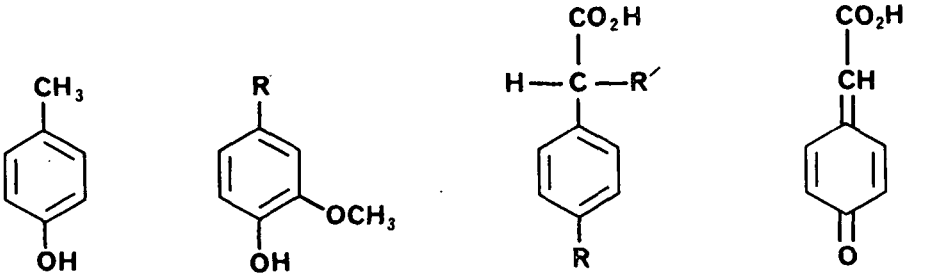
techniques not only provide information on the extent of deuteration, but also on the location of deuterium atoms. The frequency used to decouple ^{1}H-^{13}C interactions does not decouple D-^{13}C interactions during acquisition of ^{13}C-NMR spectra. A $-\overset{|}{\underset{|}{C}}-D$ group will appear as a three line signal (deuterium spins of +1, 0, -1) and at reduced intensity (poorer spin relaxation) in the ^{13}C-NMR spectrum of proton decoupled samples. A $>CD_2$ group correspondingly displays a 1:2:3:2:1 pattern of greatly reduced intensity. Thus, ^{13}C-NMR spectra show which carbons are deuterium substituted and to what approximate extent.

An experimental program was set up to examine the deuterium exchange and back proton exchange of deuterated substrates by NMR techniques to ascertain the basicity of hydroxide ion at 170°. Phenols and alcohols were frequently employed as substrates, since these compound classes are common in wood (lignin and carbohydrates).[1] The models examined here were either phenols or carboxylic acids, giving rise to soluble salts and, thus, homogeneous solutions in the aqueous alkali.

RESULTS AND DISCUSSION

Simple Phenols

Samples of p-cresol (1) and creosol (2) were completely deuterium exchanged at the available ortho and para positions by treating each with 1N NaOD in D_2O at 170° for 2 hours. [The concentrations, time, and temperature for all exchange reactions were these values, unless stated otherwise; these conditions were selected to simulate pulping conditions.] Reasonably strenuous conditions appear necessary for these exchanges, since 1 did not undergo deuteration when treated at 100° for 12 hours. The electron releasing nature of the methyl group must be partially responsible for the low reactivity, since guaiacol (3) and vanillin (4) are readily deuterated and acetovanillone (5) slowly deuterated when treated with 0.5N NaOD in D_2O at 100° for 20-24 hours.[6]



1

2, R = CH_3
3, R = H
4, R = CHO
5, R = $COCH_3$

6, R = R′ = H
7, R = OH, R′ = H
8, R = H, R′ = OH
9, R = R′ = OH

10

Phenylacetic Acids

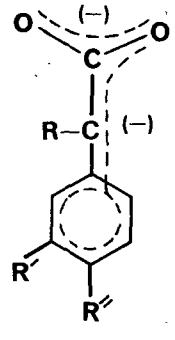
The protons on the α-carbons of phenylacetic acid (6) and p-hydroxyphenylacetic acid (7) were largely exchanged (92 and 87%, respectively, by ^{1}H-NMR) for deuteriums under the standard conditions. The ring protons ortho to the phenolic group of 7 were also exchanged (87%). Reexchange of the deuterated compounds by $NaOH/H_2O$ at 170° for 2 hours was nearly complete.

Mandelic acid (8) was also exchanged at the α-carbon position. The exact extent of exchange could not be determined from the ^{1}H-NMR spectrum because of an overlapping of the HOD and α-protons. However, the ^{13}C-NMR spectrum clearly showed extensive exchange had occurred; the C_α-carbon appeared as a weak 1:1:1 triplet, with almost no remaining -C-H singlet. [The deuterated carbons are shifted slightly upfield from the protonated carbons.] Reexchange returned the α-carbon signal back to near its original intensity.

Mandelic acids substituted with phenol groups were subjected to deuteration to determine if an additional charge on the aromatic ring would inhibit exchange at the C_α-carbon. The first compound examined, p-hydroxymandelic acid (9), gave after deuteration, a complex ^{13}C-NMR spectrum which indicated that new components were present. This result can be explained by the formation of a quinonemethide (10) and its subsequent reactions to produce undesirable by-products.[1]

The behavior of m-hydroxymandelic acid (11) to deuteration was normal; the α-proton was roughly 98% exchanged and no by-products were observed. Reexchange returned the compound to nearly its original condition. The extent of deuteration on the ortho and para ring protons were the same (67% and 77% for two separate cooks) and less than the α-proton. Figure 1 shows the ^{13}C-NMR spectra of m-hydroxymandelic acid before and after exchange. Like all others, the spectra were recorded in $NaOD/D_2O$ and therefore are of anions rather than neutral species.

In summary, the phenylacetic acid derivatives are easily deuterium exchanged at the α-carbon via carbanion intermediates which have to be multicharged species. Based on the expected acidity scale of $RCO_2H > ArOH > ROH > -CH$,[7,8] the carbanions may be as highly charged as a tetraanion (11^{-4}). Since the exchange reactions at the various acidic sites are equilibrium reactions, carbanion formation might preclude some oxyanion production. For example, the α-exchange observed with m-hydroxymandelic acid may have involved 11^{-3} rather than 11^{-4}. The probable intermediates in the exchange reactions observed for the tested phenylacetic acids are shown below.



6^-, R = R′ = R″ = H

7^-, R = R′ = H, R″ = O^-

8^{-2} or 8^{-3}, R′ = R″ = H, R = OH or O^-

11^{-3} or 11^{-4}, R″ = H, R′ = O^-, R = OH or O^-

The resonance stabilization provided to the carbanion by the carboxylate anion must be substantial. The ortho and para proton exchange reactions were less (70 vs. 98%) than α-proton exchange ion 11 and less (70 vs. 98%) than o-exchange of p-creosol. This

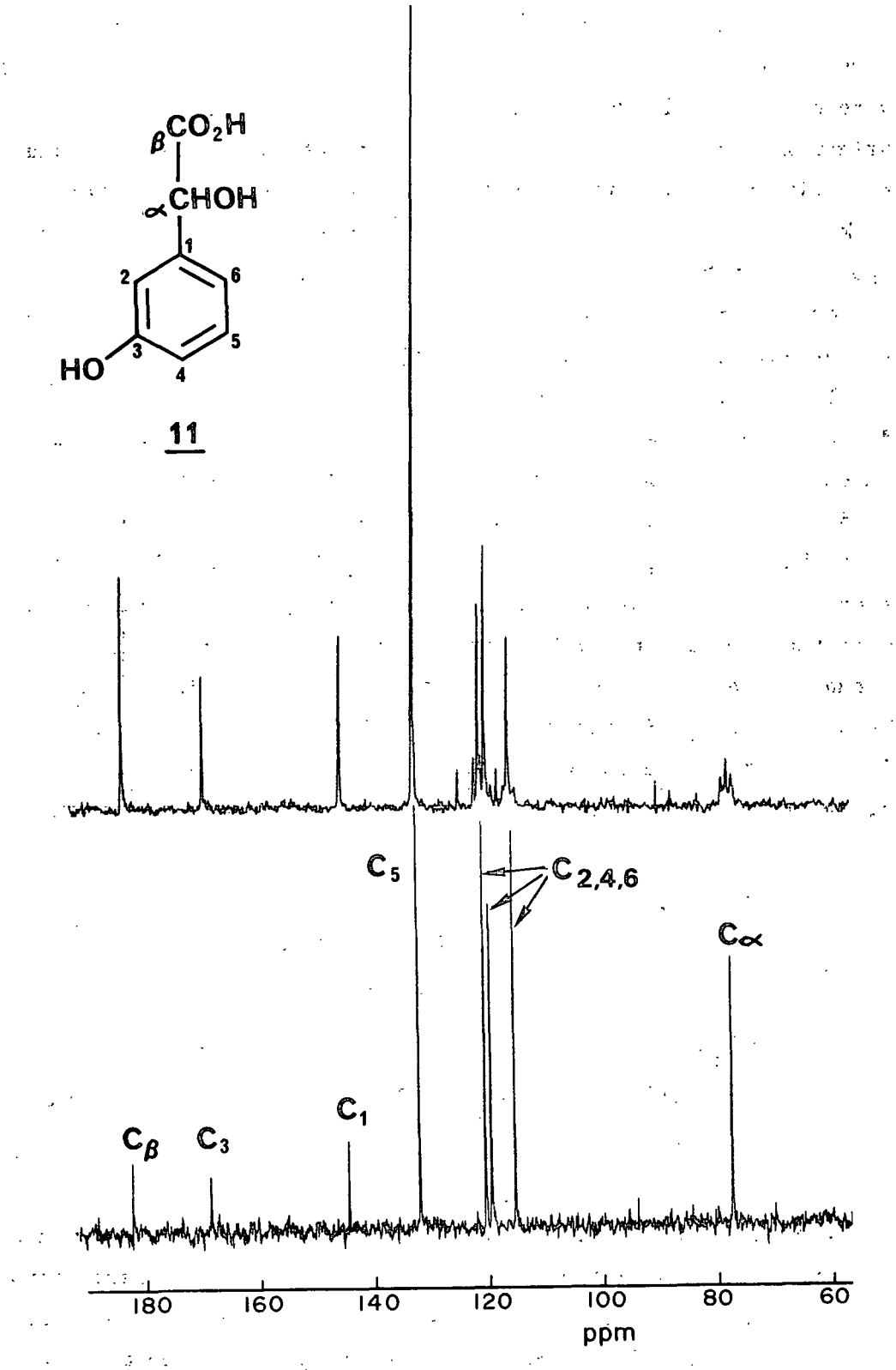
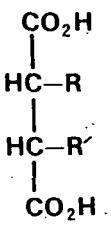


Figure 1. ^{13}C-NMR spectra of m-hydroxymandelic acid in $NaOD/D_2O$ before heating (bottom) and after 2 hrs at 170° (top).

suggests that a phenolate ion has less effect on benzyl exchange than a charged side chain has on o,p-phenol exchange. The next set of compounds examined has no aryl rings attached to the exchange site and, therefore, test the necessity of this group for stabilizing effects.

Aliphatic Carboxylic Acids

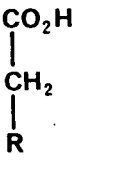
Succinic acid (12), malic acid (13) and tartaric acid (14) were completely exchanged under the standard deuteration conditions. The deuterated succinic acid was also completely reexchanged by NaOH/H2O at 170°. Some dehydration occurred with malic acid. Acetic acid (15) and glycolic acid (16) were also readily exchanged and reexchanged. However, σ-phenylvaleric acid (17) was only exchanged to about 45% and reexchange did not completely remove the deuterium atoms, 16% remained. The lower rate of exchange for 17 may be due to the electron-feeding effects of the $Ph(CH_2)_3$- group.



12, R = R′ =H

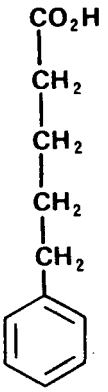
13, R = H, R′ = OH

14, R = R′ = OH



15, R = H

16, R = OH



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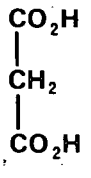
For the compounds discussed so far, the placing of a hydroxyl group on the carbanaion undergoing exchange does not retard the exchange reactions. If a hydroxyl group is ionized, it should become an electron-feeding group and, thus destabilize an attached carbanion. To answer the question of whether or not hydroxyl groups enhance or inhibit α-carbanion formation, we

investigated the exchange reactions of malonic acid (18) and tartronic acid (19).



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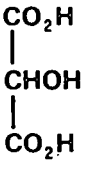

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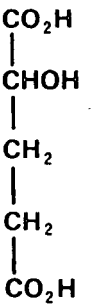

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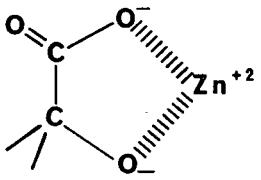
Both readily exchanged at 170°. The exchange of malonic was so rapid that it was complete in a matter of minutes at room temperature. On the other hand, 54 hours at room temperature were required to fully exchange tartronic acid. The increased resonance stability provided by the gem-carboxylic acids of 18 and 19 must account for the ease of exchange at room temperature. The difference in reactivity of the two demonstrates that an α-hydroxyl group inhibits exchange at room temperature.

The zinc salt of α-hydroxyglutaric acid (20), which has potentially exchangeable >CHOH and $-CH_2-$ groups separated sufficiently to avoid complicating dehydration reactions, was heated at 170° in $NaOH/D_2O$ and only the C_4-methylene group exchanged. Because of the insolubility of $Zn(OH)_2$, the pH may have been lower than expected. Yet, the results indicated again that an α-hydroxyl group inhibits exchange.

Could the zinc ion have played a role? Cyclic complexes, such as 21 and 22 have been postulated to be present in pulps (carbohydrates).[9] Alkaline earth hydroxides, such as strontium hydroxide, are known to increase the extent of carbohydrate "stopping" reactions.[3,10] The latter increases pulp yield. To determine the effects of zinc ion on exchange reactions, we examined the extent of C_α-H exchange for tartaric acid, with and

without zinc ion present. The aromatic protons of mandelic acid were used as an internal reference for the ^{1}H-NMR area measurements.



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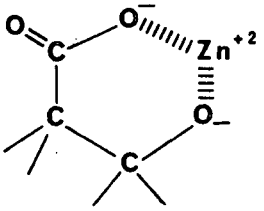

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The NaOH/D_2O exchange was performed in duplicate for 15 minutes at 170°. The amount of deuterium exchange at the alpha CHOH group was, in one case, 97.5% (no Zn^{+2}) and 90.3% (Zn^{+2}) and, in the other case, 91.4% (no Zn^{+2}) and 79.7% (Zn^{+2}). The addition of zinc ion reduced but did not prevent the exchange of an α-hydroxycarboxylic acid and suggests that divalant ions may play a role in effecting the degree of ionization with such compounds. The preferential exchange results observed for zinc α-hydroxyglutarate (20) must be largely attributed to *carbanion retardation by an* α-OH *group* rather than a zinc ion effect.

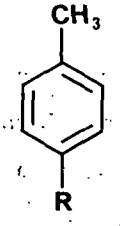
Benzyl Exchange

The exchange capacities of benzyl sites not directly attached to strong stabilizing groups were examined next. In these cases the resonance stabilization was provided by simply the attached aromatic ring or by conjugation through the aromatic ring to a carboxylic or sulfuric acid group.

Under the standard 2 hour, 170° conditions, p-toluenesulfonic acid (23) was deuterated on the methyl group to 78%; reexchange, even after 12 hours, only reduced the deuterium content to 76%. Likewise, p-toluic acid (24) was 34% deuterated in 2 hours and 5% deuterated after reexchange for 24 hours. The latter reexchange results were surprising; in general, one would expect that a low level of deuteration would dictate a low level of reexchange.

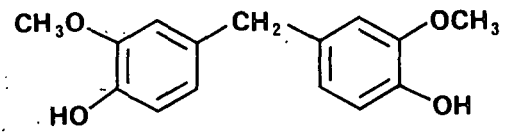
Diguaiacylmethane (25) did not undergo deuteration at 170° even after 24 hours. However, 4-hydroxydiphenylmethane (26) exhib-

ited some deuteration at 170° - 26% after 2 hours and 70% after 24 hours; reexchange over a 24-hour period reduced the deuterium content to 61%. The difference in reactivity of these two compounds can be understood by assuming that a simple aromatic ring provides some stabilizing effects to a benzyl carbanion but a phenolic ring does not. Toluene, a water insoluble compound, was not deuterated after 54 hours at 170°.



23, R = SO_3H

24, R = CO_2H



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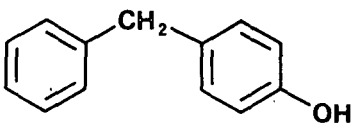

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Sodium Sulfide

The kraft pulping of wood employs sodium sulfide (Na_2S) to effect a rapid production of strong pulps.[1] It is generally assumed that the Na_2S dissociates in water to give NaOH and NaSH.[11] A simple experiment was conducted to determine the degree of dissociation and basicity of SH^- at 170°.

Three deuterium oxide solutions of p-toluic acid (24) were prepared and heated under identical conditions for 6 hours at 170°. The solutions contained 1.5 equivalents of anh. Na_2S, and 1.5 and 3.0 equivalents of NaOD, respectively. The ratios of the integrated proton NMR areas for the methyl signal relative to the aryl signals were nearly identical (0.57 and 0.58) for the solutions containing the same number of equivalents of Na_2S and NaOD, but nearly one-half (0.30) for the solution containing double the equivalents of the others. [The theoretical ratio of methyl/aryl signals for no exchange is 3/4 or 0.75.] It is apparent from these results that Na_2S is completely dissociated in water

to hydroxide and hydrosulfide at 170° and that the hydrosulfide ion is not a strong base.

CONCLUSIONS

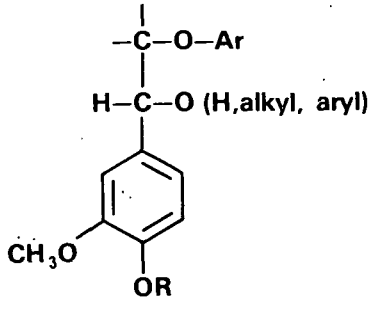
The acidity and basicity of compounds should change with temperature. As the temperature increases, a carbon acid[8] should more readily deprotonate (additional vibrational energy is imparted). Also, because of breakdown of hydrogen bonding, hydroxide ion should be less solvated and, thus, more reactive as the temperature increases. The combination of these effects probably accounts for hydroxide ion being an *apparent* very strong base at 170° in water. The acidity of the methylene protons of 4-hydroxydiphenylmethane (26) should be considerably less than that of diphenylmethane (pK_a 35)[8], and yet this substance underwent partial exchange at 170° by hydroxide ion (pK_a of H_2O is 15.74).[7,8]

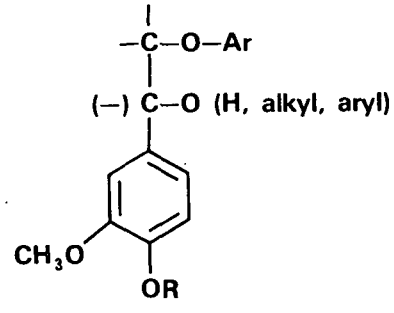
The results for the compounds tested suggest that carboxylate anions contribute significantly to the stability of a carbanion, whereas aryl groups exhibit only moderate stabilizing effects. One would have thought that the acidity of the methylene group of disodium malonate ($NaO_2CCH_2CO_2Na$) would be substantially less than that of water, since the pK_a of an uncharged analog, diethyl malonate ($EtO_2CCH_2CO_2Et$), is 13;[7] yet, all the protons of malonic acid were completely exchanged by $NaOD/D_2O$ at room temperature in a matter of minutes.

What are the implications of our results to wood chemistry problems? The reducing end of carbohydrates contains aldehyde or ketone groups and, of course, many alcoholic OH groups. The stabilization of a carbanion by an α-aldehyde or ketone group should be equal to or better (no charge-charge repulsion) than that of a carboxylate group. Since our carboxylic acid model compounds readily formed α-carbanions at 170° with hydroxide, even in the presence of several hydroxyl substituents (ArOH and ROH), carbohydrates should as well. [Actual model polyhydroxyketones and carbohydrates were not tested for fear of complications due to

reactions such as aldol condensations, eliminations, etc.]

A unit that appears often in lignin is that shown by structures 27 and 28.[1] Based on the exchange results with diguaiacylmethane (25) and 4-hydroxydiphenylmethane (26), a carbanion such as 30 would appear possible during pulping, while 29 would be quite unlikely. Carbanion 30 could undergo elimination and condensation reactions which might be contributing to "bulk delignification" and "residual lignin," respectively.[1,12]





27, R = H

28, R = alkyl

29, R = (–)

30, R = alkyl

Finally, it should be noted that the use of $NaOD/D_2O$ at high temperature in sealed metal containers offers a convenient way to deuterate mildly acidic $-\overset{|}{C}-H$ groups in compounds which are otherwise stable to alkali. Compounds such as p-toluic acid and p-toluenesulfonic acid, which only underwent partial deuteration when treated at 170° for 2 hours, could probably have been completely deuterated by raising the temperature and/or extending the time at 170°. Based on the toluene result, we suspect that water insoluble compounds can not be exchanged by our procedures. Amos and Eckert, however, have recently reported[13] that the methyl groups of 2,3- and 1,4-dimethylanthraquinone, both of which have low water solubility, can be completely deuterated in $NaOD/D_2O$ solution at 170° for 90 minutes.

The room temperature $NaOD/D_2O$ exchange of malonic acid offers a much simpler way of preparing the deuterated analog then previous methods.[14,15]

EXPERIMENTAL

Spectra were recorded on a Jeol FX-100 instrument for solutions in $NaOD/D_2O$ with the sodium salt of 3-(trimethylsilyl) propane sulfonic acid (DSS) as the internal standard. Except for diguaiacylmethane (25),[16] all compounds were commercially available.

The chemical shift and extent of exchange for many of the compounds studied are given in Tables 1 and 2. The extent of exchange of the aryl rings of the phenols examined were: p-cresol (1), ortho-98%; creosol (2), ortho-100%; p-hydroxyphenyl-acetic acid (7), ortho-87%; m-hydroxymandelic acid (11), ortho-67 to 77% and para-67 to 77% (the range is for duplicate runs).

TABLE 1

Chemical Shift and Extent Exchange at C_α of $R-\underset{R}{\overset{}{C}}HCO_2H$

R	R'	Chemical Shifts[a] α-Proton4	Chemical Shifts[a] α-Carbon	Percent Deuterium at α-carbon as given by proton NMR
H	Ph	3.52	45.91	92
H	p-OH-Ph-	3.34	46.09	87
OH	Ph	4.97	77.55	b,e
OH	p-OH-Ph-	4.56	77.19	c
OH	m-OH-Ph-	4.82	77.87	98
H	$-CH_2-COOH$	2.68	36.74	d,e
H	-CHOH-COOH	2.24-2.77	45.17	d,e
OH	$-CH_2-COOH$	4.22-4.84	56.82	d,e
OH	-CHOH-COOH	4.32	76.46	d,e
H	H	1.67	24.61	d,e
H	OH	3.68	64.70	d,e
H	$Ph(CH_3)-$	2.21	39.91	45

[a]All NMR data were acquired with $NaOH/D_2O$ solutions.
[b]Overlap of the proton signal with the HOD signal prevented a calculation of the percent deuterium by proton NMR.
[c]Formation of quinonemethide and its reactions to produce by-products made analysis by NMR impossible.
[d]The compound does not contain a nonexchangeable proton to use as a reference to calculate the percent deuterium from the proton spectrum.
[e]The carbon-13 spectrum showed that deuterium occurred to a greater extent than 90%.

TABLE 2

Chemical Shift and Extent Exchange for R-$\overset{\delta}{C}H_2$-R' (Benzyl)

R	R'	Proton	Carbon	Percent Deuterium at Benzylic Carbon
p-SO_3H-Ph-	H	2.25	23.05	78
p-CO_2H-Ph-	H	2.00	22.95	34
p-OH-Ph-	Ph	3.72	37.42	26
guaiacyl	guaiacyl	3.38	42.49	0

[a]See footnote a of Table 1.

Deuteration. - A model compound was added to 1.5 g of D_2O so that the ratio of deuteriums to all exchangeable protons was 40:1. To this was added enough 40% NaOD to completely ionize the carboxylic, sulfonic, phenolic and hydroxyl groups and then have a 1N NaOD solution left. The solution was transferred to a 5-mL bomb of moderately thick stainless steel. One to three of these small bombs were placed in a larger Parr bomb and water was added to near the top of the Parr bomb. The Parr instrument took from 30-60 minutes to reach 170 $\pm$ 3°C and was held at this temperature for 2 hours, unless stated otherwise. After the time at 170°C was complete, the Parr bomb was allowed to cool in air to room temperature. The solution was freeze-dried to remove as much HOD as possible and the proton and carbon-13 spectra obtained. An example of deuteration is given below in the case of zinc α-hydroxyglutarate.

Reexchange. - The deuterated sample and residual alkali, obtained by freeze-drying the NMR solution, were dissolved in 1.5 g of H_2O. The solution was heated, cooled and freeze-dried in the previously described manner.

Deuteration of Zinc α-Hydroxyglutarate. - The title compound (0.1985 g) was dissolved in 1.503 g of D_2O and 0.276 g of 40% NaOD in D_2O. After heating (as described above), the solution was freeze-dried and the residue dissolved in D_2O. The ^1H-NMR spectrum showed three signals: HOD at 4.78 δ, >C<u>H</u>OH at 3.85 δ as

a triplet (J ≈ 6 Hz) with shoulders, and $-CH_2CH_2-$ at 1.73 δ as a broadened singlet; the ratio of the 3.85 to 1.73 signals was 0.43. The ^{13}C-NMR spectrum showed 185.3 and 184.0 (sharp singlets, carbonyl carbons), 74.4 (sharp singlet, >CHOH), 35.5 (overlapping triplet and pentet, weak, -CDH- and $-CD_2-$) and 33.4 ppm (sharp singlet, $-CH_2-$). The ^{13}C-NMR indicates that the >CHOH group has not incorporated much, if any, deuterium. Assuming no deuterium at this position and the observed ^1H-NMR ratio of 1:2.3, we calculate that the C_4-carbon is roughly 70% $-CD_2-$ and 30% -CHD-.

Zinc Complex Deuteration. - Two solutions containing 0.0940 g (0.63 mmoles) of tartaric acid, 0.0245 g (0.16 mmoles) of mandelic acid, 0.4950 g of 40% NaOD (4.8 mmoles) in D_2O and 1.6875 g of D_2O (100 mmoles) were prepared. To one of the solutions was added 0.0530 g $ZnCl_2$. The formation of $Zn(OH)_2$ was prevented by adding the tartaric acid, mandelic acid, D_2O and $ZnCl_2$ together, dissolving the solids, and then adding the 40% NaOD. The two solutions were heated together in the Parr bomb for 15 minutes at 170°C, cooled, freeze-dried and dissolved in D_2O. The proton spectra were obtained. The integrated areas of the aryl mandelic acid and aliphatic tartaric acid signals were then compared. Ratios of 100:4 and 100:15 were observed for the nonzinc and zinc-containing solutions, respectively. Correcting for the number of protons of each type involved and the starting concentrations, we calculate that the aliphatic deuterium exchange was 97.5% (nonzinc) and 90.3% (zinc).

A repeat of this experiment gave deuterium exchange extents of 91.4% (nonzinc) and 79.7% (zinc). The difference between this latter set of data and the former pair is probably a result of differences in the time used to reach 170° and to cool back to room temperature.

Sodium Sulfide Deuteration. - Three solutions, each containing 1.5 g of D_2O and 0.1272 g (0.94 mmoles) of *p*-toluic acid, were prepared in a glove bag with a N_2 atmosphere. One of the solu-

tions also contained 0.1110 g (1.42 mmoles) of anhydrous Na_2S, another 0.14 g 40% NaOD (1.42 mmoles) and the third 0.28 g 40% NaOD (2.84 mmoles). The three solutions were heated simultaneously in the Parr bomb for 6 hours, cooled, freeze-dried, and redissolved in D_2O. Two proton spectra of each solution were obtained; the results are discussed in the text.

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